

Bioavailability of Metals in Estuarine Sediments and Their Possible Impacts on the Environment

Research Article

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Abstract

Mangroves and mudflats, important sub environments within the estuaries, are rich in nutrients and are potential sources for flora and fauna and thus provide shelter to thousands of animal and plant species. The sediments in these sub-environments composed of different geochemical phases that act as potential binding sites for metals. The metals are present in various forms and metal bioavailability includes metal species that are bio-accessible. A modified sequential extraction procedure, screening quick reference table, sediment quality guidelines as standard approaches are available to quantify different forms of metals. Our investigation revealed that Mn values are above Apparent effects Threshold (AET), indicating Mn is bioavailable and toxic to biota in mudflats of many estuaries in India. Among the trace metals Co and Zn show higher bioavailability. Distribution pattern of bioavailable metals can also be used to understand anthropogenic input to the estuaries and their mobilization.

Introduction

The coastal zone is characterized by variety of landforms like estuaries, lagoons, beaches, islands. Estuaries are one of the important sub environments of the coastal zone. Estuaries are rich in nutrients and are potential sources for flora and fauna and thus provide shelter to thousands of animal and plant species. Estuaries are coastal bodies of water, occupying an existing river valley and their characters are typified by the discharge of rivers and therefore they are regarded as complementary extensions of rivers. Estuarine regimes are governed by several factors such as river inflow, tides, waves, wind and meteorological forces making the system more complicated and dynamic thus temperature, salinity and turbidity fluctuate on daily, fortnightly and seasonal basis and reach more extremes in estuarine waters than they do at sea or in rivers.

Pritchard [1] defined an estuary as "An estuary is a semi enclosed coastal body of water, which has a free connection with the open sea, and within which sea water is measurably diluted with fresh water derived from land drainage". Estuaries are classified based on tides, as Microtidal estuaries which are formed wherever the tidal range is less than 2 m and are dominated by freshwater discharge, which leads to "salt wedge" type estuary. These are highly stratified. Mesotidal

estuaries which are formed wherever the tidal range is between 2 to 4 m. These estuaries have meandering characteristics. Macrotidal estuaries which are formed wherever there are strong tidal currents (tidal range is more than 4 m). These are trumpet in shape.

The estuaries are complex systems which receive inputs from different sources like land derived material through river, banks, marine, atmosphere etc. The river waters that mix with sea water in estuaries varies with the rate of freshwater discharge from the drainage basin and with the geological and geochemical characters of each drainage basin. Estuaries are the favourable environments of deposition of sediments derived from both the catchment area (terrestrial) and the marine sources. So, the sedimentation in estuaries is within three distinguishable regimes viz. estuarine fluvial, estuarine brackish and estuarine marine. Fine sedimentary deposits or mud are a characteristic feature of estuaries. The most significant sorting is the coarse (gravel and sand), which are found in the more energetic areas and fine (silt and clay) sediments, which accumulate in low energy conditions or quite waters. It is also necessary to mention here that the sediments are composed of different geochemical phases such as clay, silt, sand, organic material, oxides of iron and manganese, carbonate and sulphide complexes that act as potential binding sites for metals entering an estuarine system. In the sediments, metals can

be present in various forms and generally exhibit different physical and chemical behaviour in terms of chemical interactions, mobility, biological availability and potential toxicity. Therefore, the fate of various metals, in the natural environment is of great concern. Metals may be partitioned into six fractions: dissolved, exchangeable, carbonate, iron-manganese oxide, organic, and crystalline. The metal bioavailability includes metal species that are bio-accessible and are absorbed or adsorbed by an organism with the potential for distribution, metabolism, elimination, and bioaccumulation.

Methods

The sediment samples may be surface and/or subsurface can be collected from sub-environments like mudflats, mangroves etc. within estuaries using a hand driven PVC coring tube. Representative of each sub-sample can be powdered by using an agate mortar and pestle for geochemical analysis. A modified sequential extraction procedure [2] can be adopted to quantify the metals in different operationally defined geochemical phases. The steps involved in separating the phases are detailed below.

Fraction 1: It is a soluble / exchangeable fraction in which the contaminants are weakly adsorbed to the clays and organics in the sediment via electrostatic attraction. From a biological availability point of view, metals in this fraction are readily available [2]. Magnesium chloride is an effective reagent for desorbing adsorbed trace metals.

Fraction 2: In this fraction the contaminants are bound to carbonates. The metals are very susceptible to changes in temperature and pH of the solution and therefore the next most readily available [2]. Buffered acetic acid and sodium acetate was applied to leach the metals in this fraction.

Fraction 3: In this fraction the contaminants are bound to Fe and Mn oxy- hydroxides. They exist in sediment as cement, nodules and concretions and tend to be thermodynamically unstable in anoxic conditions. They are most susceptible to changes in Eh (increased availability at low Eh). These contaminants are most biologically available under reducing conditions [2].

Fraction 4: The contaminants here are bound to various forms of organic matter with strong bonds. Metals in this fraction may be associated with organic matters, such as organic coatings on inorganic particles including biotic detritus. Under oxidising conditions, these contaminants are released upon degrading the organic matter. Contamination in the Organic matter fraction is the least biologically available [2] among the first four phases. Stability of the metals in this fraction is high when compared with above three fractions and thus incorporation in geochemical cycle is difficult. Hydrogen peroxide in acid medium used to oxidise organic matter whereas, Ammonium acetate is used to prevent adsorption of extracted metals on the oxidized sediment.

Fraction 5: Residual fraction includes metals incorporated into the crystal structure of the primary and secondary minerals. These contaminants are not biologically available and can only be released with the use of a very strong acid such as HF [2,3]. Metals in this fraction are inert and may not take part in the biochemical or chemical reactions under normal environmental conditions.

The fractions can be digested in Teflon beakers using the combination of HF, HClO₄ and HNO₃. The digested samples can be analyzed for various metals on Varian 240FS model Atomic

Discussion

In recent years, there has been increasing concerns about pollutants entering the aquatic environment. A need to discover simple and reliable pathways to monitor levels of particular metals or other pollutants in the aquatic environment has resulted in a proliferation of studies. Jonathan et al. [4] studied recent sediments off Gulf of Mannar along the southeast coast of India and their studies revealed the enrichment of Cr, Pb, Cd, Cu, Ni, and Zn and indicated that the area has been contaminated by riverine sources and industries nearby. Alagarsamy [5] had studied the seasonal distribution of trace metals such as Fe, Mn, Co, Cu, Zn and Pb in the Mandovi Estuary, west coast of India. His results revealed that the surface sediments of Mandovi Estuary are moderately or strongly contaminated to some extent by Fe and Mn. Cu and Zn showed the influence of organic wastes from municipal sewage entering into the estuary, in the river mouth region. Janaki - Raman et al. [6] have reported that the trace metals in sediments of Muthpet mangroves, South - East Coast of India are diagenetically modified and anthropogenic processes control Pb and to some extent Ni, Zn and Fe. Nayak et al. [7] have studied the abundance and distribution of total suspended matter (TSM) from Mandovi and Zuari estuaries in three different seasons over the last seventeen years. They have reported that in Zuari estuary, TSM concentration increased in both surface and bottom waters from year 1991 to 2004. Recently, Department of Marine Sciences of Goa University under the research project "Reading pollution history, paleoclimate and sea level changes from the study of mudflats, central west coast of India" has carried out a detailed study on mudflats along central west coast of India [8-11].

Mud deposition is characteristic of protected low energy environments such as estuaries and lagoons. This occurs in the intertidal zone where regular and increased depth of flooding prevents salt tolerant plants growing. Intertidal mudflats are a prominent geomorphological component of estuaries and the development of an estuarine mudflat is both complex and difficult to predict because of the multiple relationship between the physical, chemical and biological properties of the sediment. Further, due to their potential role as contaminant storage areas, mudflats tend to release heavy metals into the estuarine waters by various chemical, physical and biological processes which may facilitate mixing and remobilization [10].

Speciation of metals is the identification of metals that are bound to different components of the sediment [12] and the phases have been defined [2,13]; as exchangeable ions, adsorbed ions / carbonates, Fe and Mn oxides, sulphides / organics and metals bound to lithogenic minerals and residual. Bioavailable metal fractions include Exchangeable fraction which consist of metals bound to colloidal or particulate material. Generally, clay and organic matter controls ionic exchange thus responsible for availability of metal in exchangeable metal form. Further it is understood that pH plays an important role in governing concentrations of soluble metals. Mn solubility is low at high pH and with high organic matter content, while in acid soils with

low organic matter its solubility and availability is high. The solubility of Mn is high at pH above 6 in anaerobic condition. Metals associated with carbonate minerals constitute the carbonate fraction, which can be newly precipitated in soil. The element in carbonate fraction would be released more into the environment if the conditions became more acidic. The co-precipitation with carbonate minerals is of importance for a number of metals in addition to Mn which includes Zn and Pb. The iron-manganese oxide fraction consists of metals adsorbed to iron-manganese oxide particles or coatings. Fe-Mn oxide fraction includes the metal oxides/hydroxides soluble under slightly acidic pH, as well as the metals associated with reducible amorphous Fe-Mn Oxy-hydroxides. Metals from this fraction are released into the environment with a decrease in pH and if sediments change from oxic to anoxic condition. The organic fraction consists of metals bound to various forms of organic matter. Most metal hydroxide minerals have very low solubility under pH conditions in natural water. Adsorption, which occurs when dissolved metals are attached to surfaces of particulate matter (notably iron, manganese, and aluminium oxide minerals, clay, and organic matter), is also strongly dependent on pH and, of course, the availability of particulate surfaces and total dissolved metal content. Therefore, organic matter/Sulphide fraction represents the amount of metals bound to the organic matter and sulphides that would be released into the environment if conditions became oxidative. However, the intensity of complexation is found to vary progressively with the metal concentration, with high-intensity sites being filled first, followed by sites of lower intensity. Residual fraction named as inert phase, corresponds to that part of the metal, which cannot be mobilized.

Dessai and Nayak [14] had studied speciation of metals in Zuari estuary and reported that Mn and Co are higher in concentration in exchangeable fraction. Li et al. [15] had studied the metal distribution in the coastal wetland of the Pear River Estuary, China, and they have reported higher content of Cd and Zn in the exchangeable fraction indicating their ecological risk. Farkas et al. [16] had studied chemical speciation by using sequential extraction procedure and

also evaluated geoaccumulation Index of the sediments to assess the heavy metal pollution in surface sediments of the River Po.

Further, Buchman [17] introduced Screening Quick Reference Table (SQUIRT) for metals in marine sediments, which can be used as a standard to declare the given estuarine sediments have reached the threshold with respect to pollution of metals. Screening Quick Reference Table (SQUIRT) developed by (NOAA) is presented in Table 1. Based on SQUIRT, the guideline values are categorized into five classes which are also presented in the Table 2.

TEL: Threshold effect level; ERL: Effect range low; PEL: Probable effects level;

ERM: Effect range median; AET: Apparent effects threshold

(Except for Fe, all values are in ug/g)

When the speciation data is compared with SQUIRT (Table 1), Mn shows values above AET indicating Mn is bioavailable and toxic to biota in mudflats of many estuaries in India. Among the trace metals Co and Zn show higher bioavailability.

The metals in acid soluble fractions are considered to be the weakest bonded metals in sediments which may equilibrate with the aqueous phase, and thus become more easily bioavailable [18]. Thus, metal speciation is of critical importance to their potential toxicity and mobility [19]. A criterion called "Risk Assessment Code (RAC)" has been used to assess the potential mobility and hazard of metal based on the percentage of exchangeable and bound to carbonate metal in the sediment [20,21]. The metals in different fractions are bound with different strengths in the sediments. If a sediment sample can release in these fractions less than 1% of the total metal, it will be considered safe for the environment. On the contrary, sediment releasing in the same fractions more than 50% of the total metal has to be considered highly dangerous and can easily enter into the food chain. The classes based on RAC is given in Table 3.

Our studies have shown class III to V RAC for Mn, Co and Pb

Table 1: Screening quick reference table for metals in marine sediments [17].

ELEMENTS	TEL	ERL	PEL	ERM	AET
Fe	-	-	-	-	22% (Neanthes)
Mn	-	-	-	-	260 (Neanthes)
Cu	18.7	34	108	207	390 (Microtox & oyster larvey)
Zn	124	150	271	410	410 (Infaunal community)
Cr	52.3	81	160	370	62 (Neanthes)
Co	-	-	-	-	10 (Neanthes)

Table 2: Sediment guidelines and terms used in SQUIRT.

Sediment guidelines	
Threshold Effect Level (TEL)	Maximum concentration at which no toxic effects are observed
Effects Range Low (ERL)	10 th percentile values in effects or toxicity may begin to be observed in sensitive species
Probable Effects Level (PEL)	Lower limit of concentration at which toxic effects are observed
Effects Range Median (ERM)	50 th percentile value in effects
Apparent effects Threshold (AET)	Concentration above which adverse biological impacts are observed

Table 3: Criteria of Risk Assessment code [20].

Grade	Sum of exchangeable and carbonate in % of the total	RAC
I	<1	No risk
II	1-10	Low risk
III	11 – 30	Medium risk
IV	31 – 50	High risk
V	>50	Very high risk

in some of the estuaries along west coast of India. The bioavailability of Mn is higher with organic fraction as a major phase in some areas. Mn association with carbonate fraction shows its ability to replace calcium in carbonate minerals as a result of their similar ionic radii and charges. Mn is also higher near surface compared to subsurface. This could be due to Mn remobilization from the reducing deeper sediment sections and accumulation in oxidized surface sections. Distribution pattern of bioavailable metals can also be used to understand anthropogenic input to the estuaries and their mobilization.

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